

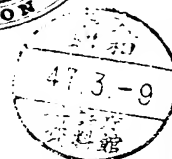
1259910

PATENT SPECIFICATION

(11) 1259910

NO DRAWINGS

- (21) Application No. 14764/70 (22) Filed 26 March 1970
 (45) Complete Specification published 12 Jan. 1972
 (51) International Classification C 08 g 5/06, 7/00 // 37/06, 51/02
 (52) Index at acceptance
 C3R IC11 IC14B IC17A IC22 IC4 IC6X ID1A1 ID1AX
 1E1A 1E2A 1L1A 1L5X 1L6D 1N1H 1N1MX 1N2C
 (72) Inventors NATALIA VLADIMIROVNA SHORYGINA, IOSIF
 LEONIDOVICH KLIPINITSER, TATIANA
 ALEXANDROVNA POPOVA, VYACHESLAV
 KUZMICH NININ, NATALIA VASILIEVNA
 ZHILINA, NATALIA ALEXEEVNA
 CHUROCHKINA, VLADIMIR SERGEEVICH
 SAVIN, IRAIDA ALEXEEVNA PUCHKOVA,
 GENNADY GEORGIEVICH POPOV, VALENTINA
 MIKHAILOVNA BORODINA, EVGENIA
 MITROFANOVNA TESLENKO, FRIDA
 ZALMANOVNA SOKHOR, BELLA SIMONOVNA
 GRACHEVA, GRIGORY VASILIEVICH
 KHOMUTINKIN, IOSIF ARONOVICH
 LEVANTOVICH, ANATOLY ABRAMOVICH
 KRUGLIKOV and ZOYA YANOVNA EIFLER



(54) A METHOD OF PRODUCING ARYLENEPHENOL-
 FORMALDEHYDE RESINS AND MOULDING MATERIAL
 ON THE BASIS THEREOF

(71) We, NAUCHNO-ISSLEDOVATEL-
 SKY INSTITUT PLASTICHESKIKH MASS, a State
 Enterprise, organised and existing under the
 Laws of the Union of Soviet Socialist Repub-
 lics, of E-112, Moscow, Union of Soviet Social-
 ist Republics, do hereby declare the invention
 for which we pray that a patent may be
 granted to us, and the method by which it is
 to be performed, to be particularly described
 in and by the following statement:—

The present invention relates to methods
 of producing arylene phenol - formaldehyde
 resins (phenoformolites) containing aromatic
 hydrocarbons. Phenoformolites belong to the
 class of thermosetting resins and can harden,
 passing into three-dimensional infusible in-
 soluble structures.

It is also an object of the invention to em-
 ploy the obtained phenoformolites in the pro-
 duction of a moulding material.

Known in the art are a number of two-stage
 methods of producing phenoformolites, com-
 prising synthesizing formolites by condensation
 of aromatic hydrocarbons with formaldehyde in
 strongly acidic media (25—45% H_2SO_4), and
 subsequently synthesising of the phenoformo-
 lites by condensing the washed neutralized
 formolites with phenol and an additional
 amount of formaldehyde.

Also known is a method of producing pheno-
 formolites by the cocondensation of reactive
 aromatic hydrocarbons with phenol and form-
 aldehyde. The process is carried out in the pre-
 sence of sulphuric and hydrochloric acid, the

[Price 25p]

concentration of which at the end of the re- 35
 action should be not less than 15—20%.

The disadvantages inherent in the known
 methods are as follows.

The necessity to dispose of tremendous
 amounts of spent sulphuric acid, as well as to 40
 wash and neutralize formolites; the necessity
 of employing special acid-resistant equipment
 and communications, both for the two-stage
 and single-stage methods; the impossibility of
 using polycyclic hydrocarbons which feature a 45
 high melting point, *per se*, such hydrocarbons
 being usually used in the form of solutions in
 liquid aromatic hydrocarbons.

The object of the present invention is to
 obviate or mitigate the above disadvantages. 50

According to the invention there is provided
 a method of producing an arylene phenol-
 formaldehyde resin, comprising condensing a
 eutectic or natural polyeutectic mixture of
 aromatic hydrocarbons with phenol and form- 55
 aldehyde in the presence of an acid catalyst.

The reactivity of said mixtures is close to
 that of phenol, as has been shown by the in-
 vestigation of the initial rates with which these
 mixtures react with formaldehyde. The close 60
 reaction rates of eutectic and natural poly-
 eutectic mixtures of hydrocarbons and phenol
 with formaldehyde make it possible to effect
 the process in one stage, obviating the need to
 separate the formolite. 65

Moreover, the method of the present inven-
 tion makes it possible to considerably reduce
 the consumption of the acid catalyst and to

use high-melting aromatic hydrocarbons and technical mixtures of aromatic hydrocarbons (natural polyeutectic mixtures) which have not been employed heretofore.

- 5 Since the melting point of eutectic mixtures is considerably lower than the melting point of individual hydrocarbons, the method of producing phenoformolites proposed herein enables the use of practically any hydrocarbon of the aromatic series.

- 10 As eutectic mixtures use may be made, for example, of mixtures of pyrene and fluoranthene, pyrene and naphthalene, pyrene and coronene, naphthalene and phenanthrene. In addition to artificial mixtures it is also possible to employ technical mixtures which are complex polyeutectic systems, such as crude anthracene.

- 20 The ratio between the eutectic or polyeutectic mixture, phenol and formaldehyde may be varied within a wide range. Most expedient in this respect prove to be weight ratios equal to 1:1—2:0.287—0.575, (from 1:1:0.287 to 1:2.0:575).

- 25 An acid catalyst is recommended to be taken in the process in an amount equal to 0.1—2% of the total weight of the reagents.

- 30 If eutectic or polyeutectic mixtures whose melting point is below 100°C are used, it is advisable to use formaldehyde in the form of a 35—38% aqueous solution thereof.

- 35 If the eutectic mixtures used have a melting point above 100°C, it is recommended that formaldehyde oligomers should be employed as the source of formaldehyde.

- 40 Phenoformolites produced by the present method may be successfully used as a binder in the production of both general-purpose moulding material which require organic fillers, such as wood flour, and special-purpose moulding material containing mineral fillers. The composition of the moulding material is made in accordance with conventionally adopted formulations, and the ratio between the ingredients in this composition (a binder, organic or mineral fillers and hardeners) is within the generally known adopted ranges. The moulding material based on phenoformolites may be formed into articles by press moulding or injection moulding. The presence in phenoformolites of aromatic hydrocarbons with con-

densed nuclei makes it possible to produce articles featuring high dielectric and thermo-physical characteristics.

The method proposed herein may be carried out without any additional capital investments, on existing equipment employed in plants producing plastics, and in accordance with the flow sheets now in use. The employment of small amounts of catalysts makes it unnecessary to utilize special acid-resisting equipment.

For a better understanding of the present invention, given hereinbelow are examples illustrating the producing of arylenephenol-formaldehyde resins and their application.

EXAMPLE 1

A vacuum cooker is charged with 19.6 parts by weight of fluoranthene, 8.4 parts by weight of pyrene, 42 parts by weight of phenol, 9.6 parts by weight of α -polyoxymethylene and 0.5 part by weight of $ZnCl_2$. The condensation is carried out at 95—100°C with constant stirring for 5 hours. The resin obtained is vacuum-dried and drained.

EXAMPLE 2

A three-necked flask equipped with a reflux condenser, a thermometer and a stirrer is charged with 22.4 parts by weight of coronene, 5.6 parts by weight of pyrene, 56 parts by weight of phenol, 15 parts by weight of α -polyoxymethylene and 1 part by weight of $ZnCl_2$. The polycondensation is carried out at a temperature of 105—110°C with constant stirring for 5 hours. The resin obtained is discharged into an evaporating dish and dried.

EXAMPLE 3

A vacuum cooker is charged with 20 parts by weight of crude anthracene, 40 parts by weight of phenol, 35 parts by weight of formalin (36.7%) and 1 part by weight of hydrochloric acid (sp. gr. 1.19). The reaction mass is heated up to the boiling point with constant stirring and kept at a temperature of 95—100°C for 2 hours, whereupon the resin is dehydrated under a vacuum and drained.

The properties of the phenoformolites obtained in the above Examples are listed in Table 1.

TABLE 1

Characteristics	Phenofomolite based on crude anthracene	Phenofomolite based on eutectic mixture of fluoranthene and pyrene	Phenofomolite based on eutectic mixture of coronene and pyrene
Rate of gelation on plate at 160°C with 10% of urotropin, sec.	60—80	80—90	60—70
Amount of extracted substances in alcohol-benzene mixture, 1:1, per cent	2—3	2—3	2—3
Coking index, per cent	60—63	65—67	70—72
Ubbelohde drop point, °C	110—120	104—106	110—115
Losses in weight when testing on derivatograph:			
100°C	0	0	0
200°C	0	0	0
300°C	1.9	1.7	1.1
400°C	5.5	5.3	4.2
500°C	23.7	23.2	20.8

EXAMPLE 4

On the basis of the phenofomolites produced as described in Examples 1—3 compositions are prepared, comprising (in per cent by weight): phenofomolite (resin) — 42.8, urotropin — 6.5, kaolin — 1.5, — nigrosine — 1.5, lime — 0.9, stearine — 0.7, wood flour — 43.2. The compositions are rolled on continuous-action rolls with the gap therebetween equal to 1—2 mm. The resulting sheets of the rolled material are comminuted and used for press moulding.

The properties of the moulding materials produced as described in Example 4 are presented in Table 2.

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TABLE 2

Characteristics	Moulding material based on resin made from crude anthracene	Moulding Material based on resin made from fluoranthene and pyrene	Moulding Material based on resin made from coronene and pyrene
Specific impact strength, kg.cm/cm ²	6.5	5.5	5.9
Static bending strength, kg/cm ²	749	758	773
Brinell hardness, kg/mm ²	65	66	71
Martens thermostability, °C	187	186	189
Water absorption, per cent	0.018	0.013	0.009
Surface resistance, ohm	2.9×10^{15}	2.8×10^{15}	3.8×10^{15}
Volume resistance, ohm.cm	3.7×10^{11}	3.7×10^{11}	4.5×10^{11}
Dielectric constant	4.5	4.5	4.9
Dielectric power factor	0.025	0.022	0.017
Average breakdown voltage, kV/mm	14.8	15.3	15.9

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WHAT WE CLAIM IS:—

1. A method of producing an arylene phenol-formaldehyde resin, comprising condensing a eutectic or natural polyeutectic mixture of aromatic hydrocarbons with phenol and formaldehyde in the presence of an acid catalyst.
2. A method as claimed in claim 1, wherein the condensation is carried out with the weight ratios between the eutectic or natural polyeutectic mixture of aromatic hydrocarbons, phenol and formaldehyde being equal to 1:1—2:0.287—0.575 (1:1:0.287 to 1:2:0.575).
3. A method as claimed in claims 1 and 2, wherein the amount of acid catalyst used is from 0.1 to 2% of the total weight of the reagents.
4. A method as claimed in claims 1, 2 or 3 using a eutectic or natural polyeutectic mixture with a melting point below 100°C, wherein formaldehyde is employed in the form of a 35—38% by weight aqueous solution thereof.
5. A method as claimed in claim 1, 2 or 3, using a eutectic mixture with a melting point above 100°C, wherein formaldehyde oligomers are used as the source of formaldehyde.
6. A method of producing an arylene phenol-formaldehyde resin according to any one of the Examples.
7. Arylene phenol-formaldehyde resins whenever produced by the method claimed in any one of claims 1 to 6.
8. A moulding material including as a binder, an arylene phenol-formaldehyde resin as claimed in claim 7.
9. A moulding material according to claim 8 including also an organic or mineral filler and a hardener to produce a material suitable for injection or press moulding.

H. D. FITZPATRICK & CO.,
Chartered Patent Agents,
14/18, Cadogan Street, Glasgow, C.2. and
27, Chancery Lane, London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.